The Effect of Powders on Premixed Hydrocarbon-Air Combustion[*]

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I. Introduction

It has long been known that finely powdered salts such as $NaHCO_3$ can be used to extinguish fires or to prevent ignition of combustible gaseous mixtures. Various studies (Ref. 1) of combustion inhibition have revealed that powdered materials vary widely in their ability to inhibit combustion, that alkali metal salts are generally effective inhibitors, and that the effectiveness of at least some powders is proportional to the specific surface area of the material (Ref. 2). The available data do not permit identification of the significant processes which result in inhibition. The present study of combustion inhibition by finely divided powders was undertaken in order to elucidate the mechanism of flame inhibition.

II. Experimental Details and Results

A. Materials

Various gases were used as obtained from commercial sources. These included C.P. CH_4, C_3H_8, NH_3, and A from the Matheson Co., industrial grade O_2, commercial dry N_2 from General Dynamics Corp. Compressed laboratory air was dried prior to use by passage through a bed of granular $CaCl_2$.

All the powders used were C.P. anhydrous materials. Some were of sufficient fineness to be used as received; most, however, required some size reduction. These were wet milled with acetone in a small laboratory ball mill. After milling, the powder was first air dried under a heat lamp to remove the bulk of the acetone and then oven dried at about 110°C. The dry powder cake was pulverized by brief ball milling and then sieved through a 250 or a 325 mesh stainless steel screen. Most of the test powders were used without further treatment.

Milled powders contained a wide range of particle sizes. Two methods of size separation were tried, sieving and gas elutriation. Attempted sieving by means of micromesh screens was unsuccessful because the screens plugged quickly. Gas elutriation with dry N_2 was inefficient and slow except at high gas flow rates. Some size reduction could be obtained but not as much as desired. Consequently, gas elutriation was used only for special purposes and not as a standard procedure.

B. The Dispersal of Powder in a Combustible Gas

A dispersing device was assembled for the introduction of powders into combustible gas mixtures which performed adequately for most cases. The powder

generator (Fig. 1) consisted of a Pyrex cylinder (6 cm i.d.) fitted at each end with large rubber stoppers. The generator was provided with five jets through which gas could enter the system, a four-bladed propeller to agitate the powder bed, and an exit tube for the gas-powder mixture. The propeller was driven by a 1500 RPM electric motor. Four of the gas jets were made from glass tubing and had an opening of about 1 mm in diameter. The fifth jet, used only to obtain high powder concentrations, was made from brass tubing with a hemispherical cap through which five holes 0.015 inch in diameter had been drilled. One of these holes was on the axis of the tube, the other four were arranged symmetrically around it. The gas emerging from these holes was very effective in picking up powder from the powder bed.

In order to introduce the powder into the gas mixture a steady flow of premixed fuel and oxidizer of known composition from a conventional gas handling system was split by means of needle valves into two streams; one passed directly to the vertical output tube of the powder generator, and the other entered the powder generator through the glass jets. The concentration of powder in the final mixture could be changed by varying the relative amounts of the two gas streams up to the point when all of the gaseous mixture passed through the generator. If even higher powder concentrations were desired, it was again necessary to split the gas flow, this time into a fraction which entered the generator through the four glass jets and the remainder through the metal jet. In this manner it was possible to obtain powder concentrations up to about 10% by weight of the gas flow.

C.   Measurement of the Effect of Powder on Combustion

The effectiveness of the powder was determined from the change in flame propagation velocity as measured in the apparatus shown in Fig. 1. A long glass cylinder, about 2 cm in diameter, was inserted a short distance into the generator. The gas-powder mixture from the generator flowed vertically upward through the tube and was vented to the atmosphere at the top. After a steady flow of gas-powder mixture had been established, the powder output was measured by collecting on a glass filter paper* the powder content of the gases. A collection time of 30 or 60 seconds was usually sufficient to give a weighable amount of powder on the filter. The weight concentration of powder in the gas was calculated from the collection time, the weight of collected powder, and the flow rate of the gas stream. Immediately after a powder sample had been collected, the flow of gas was stopped, the damper valve closed, the side vent opened to the atmosphere, the top of the tube capped with a rubber stopper, and the mixture ignited by spark. The time required for the flame to travel between two fixed points on the tube was measured by phototubes. The phototube signals were displayed on an oscilloscope face and photographed by Polaroid camera. The average propagation velocity of the flame was calculated from the known distance between the phototubes and the measured time of transit.

In the absence of powder the flames were approximately hemispherical in shape; after the first few inches of travel, they moved through the tube at an apparently uniform rate. Slight tilting of the flame was sometimes observed. The presence of powder at times resulted in irregular flame shapes. Because the propagation velocity v is related to flame speeds by $v = SA_f/A_t$ (where A_f = the area of the flame and A_t = cross-sectional area of the tube), these perturbations of flame shape are a source of error. In extreme cases the flames were extremely long and highly tilted, as a result of nonuniform powder distribution in the tube.

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*Mine Safety Appliance Co.

D.   Measurement of Particle Size and of Specific Surface Area

Specific surface area of the experimental powders was measured by an optical method (Ref. 3). About 20 mg of powder was thoroughly dispersed in about 300 ml of acetone contained in an optical cell and the optical density of the mixture measured. The total specific area of the powder, $A*$, was calculated from the approximate relation

$$A* = \frac{-4\ln \xi_i}{2cl} \tag{1}$$

where ξ_i = the initial optical transmission, c = the powder concentration in gms/cc, and l = optical path length (5 cm in this case).

When size analysis was desired, the optical density was recorded for a period of time sufficient for settling of the powder suspension. The distribution of particle sizes can be derived from the chart record of $-\ln\xi$ vs. time (Refs. 3 and 4).

The specific surface data listed in Table I were obtained in the manner described. The average particle size, $\bar{d}$, is defined by Eq. 2

$$\bar{d} = \frac{6}{\rho A*} \tag{2}$$

where ρ is the density of the powder material. One gram of powder containing only particles of diameter $\bar{d}$ would have the same surface area as one gram of the actual powder. Size analysis revealed that $\bar{d}$ is only a crude measure of powder fineness. All powders listed in Table I, even the coarse ones, contained a substantial number of particles with diameters of only 2 or 3 microns. For example, the weight distribution of NaF particles passed through a maximum at about 3.5μ although $\bar{d} = 6.5\mu$.

The data in Table I refer to samples collected at the exit of the flame tube. Comparison of that data with surface data for the powder initially present in the generator revealed little or no difference for fine powders ($A* \approx 10,000$ cm^2/gm). For coarse powders the material collected at the burner tube was finer than the original powder charge. It appears that the generator also functioned to some extent as an elutriation device. To avoid error from such elutriation only a few per cent of the initial powder charge in the generator was used in a related series of measurement.

E.   The Effect of Powders on Premixed Flames

Several of the powders tested were not effective inhibitors of premixed CH_4-air combustion. About 5 wt % of CaF_2, talc, $CaCO_3$, or $Ca(OH)_2$ was required to reduce by 10% the speed at which a stoichiometric CH_4-air flame propagated through a tube. Heat and momentum loss by the flame are sufficient to account for that degree of reduction. On the other hand, the remainder of the powders tested, NaF, NaCl, NaBr, CuCl, K_2SO_4, $NaHCO_3$, $KHCO_3$, and Na_2CO_3 were effective inhibitors of CH_4-air combustion to a degree which indicates chemical interference with the combustion process.

As shown in Fig. 2, relatively little Na_2CO_3 is required to produce a significant reduction in the propagation velocity of a stoichiometric CH_4-air flame. These following features should be noted: (a) the weight concentration of powder when expressed in mg/cc is very nearly the same as the weight fraction; (b) the scatter in the data is primarily due to perturbations of flame shape; (c) the ratio of flame area to tube, apart from erratic perturbations, increases from about 2 at zero inhibitor concentration to about 4 at concentrations corresponding to points on the nearly horizontal portion of the curve; (d) the powder concentration corresponding to the intersection of the dotted straight lines may be used as

a measure of inhibitor effectiveness. The lower this critical concentration, the more effective the inhibitor. For fine Na_2CO_3 this intercept concentration is about 0.6 wt % whereas for the coarser Na_2CO_3 the intercept concentration is about 1.1 %. Comparison of these values with the specific surface area of the two powders indicates that powder effectiveness is approximately proportional to specific surface area.

As shown in Fig. 3, similar results were obtained using $NaHCO_3$. Because of flame perturbations for low concentrations of $NaHCO_3$, the relation between powder effectiveness and A* could not be determined with precision. However, a size effect is clearly evident. In view of the fact that $NaHCO_3$ decomposes to Na_2CO_3 at relatively low temperature, it is probable that the observed effectiveness of $NaHCO_3$ merely reflects the effectiveness of Na_2CO_3 . The data shown in Figs. 2 and 3 are consistent with this interpretation. The effect of $KHCO_3$, A* = 12,400 cm^2/gm, on propagation velocity is shown in Fig. 4. Comparison with the data for $NaHCO_3$, A* = 11,900 cm^2/gm , reveals that $KHCO_3$ powder is twice as effective as $NaHCO_3$ powder. It is noteworthy that $KHCO_3$ has been found to be twice as effective as $NaHCO_3$ as a fire extinguisher (Ref. 5). Because both $NaHCO_3$ and $KHCO_3$ decompose readily to the respective carbonates, the effective inhibitor in both cases is probably the alkali carbonate. The effectiveness of $NaHCO_3$ for non-stoichiometric CH_4-air mixtures (CH_4 from 8 to 12 % by volume) was comparable with or slightly greater than for the stoichiometric flame.

The effect of NaBr , NaCl , NaF , CuCl , and K_2SO_4 on stoichiometric CH_4-air flames was also measured. Precise results were obtained for NaCl and CuCl (Figs. 5 and 6). Qualitatively NaBr, NaF , and K_2SO_4 were also effective inhibitors, but because of extreme flame instability precise data could not be obtained. This instability is apparently associated with poor dispersibility of the powder.

Flame inhibition by dispersed powder is affected by oxidizer concentration. A Stoichiometric CH_4-O_2 flame diluted with N_2 so that $O_2/(O_2 + N_2)$ = 0.25 required 1.7 wt % of fine Na_2CO_3 to reduce the linear speed from 142 cm/sec to the intercept point which in this case occurs at about 20 cm/sec. The increase in powder requirement reflects primarily the higher initial propagation velocity. Support for this view is provided by another experiment using a CH_4-O_2-A mixture with an initial propagation velocity very nearly the same as that for a stoichiometric CH_4-air flame, 65 cm/sec. The effectiveness of $KHCO_3$ in the two cases was much the same, about 0.6 wt % powder. In contrast, the presence of about one per cent by volume of CH_3Cl in a stoichiometric CH_4-air mixture considerably reduced the effectiveness of Na_2CO_3 although the CH_3Cl itself has very little effect on the initial propagation velocity of the mixture (see Fig. 7).

The effectiveness of Na_2CO_3 (or $NaHCO_3$) was found to vary with the nature of the fuel. About 2.5 wt % of Na_2CO_3, A* = 10,800 cm^2/gm, was required to reduce the propagation velocity of a stoichiometric C_3H_8-air flame from 80 cm/sec to 20 cm/sec, compared to about 1 wt % for a stoichiometric CH_4-O_2-N_2 mixture of the same initial propagation velocity. The noncarbonaceous system NH_3-O_2-N_2 was found to be only slightly affected by powdered $NaHCO_3$. For a near stoichiometric composition with an oxidizer concentration $O_2/(O_2 + N_2)$ = 0.4, two wt % of $NaHCO_3$, A* = 11,980 cm^2/gm, only reduced propagation velocity from 62 cm/sec to 52 cm/sec.

III. The Temperature History of Small Particles Exposed to a Premixed Flame

During passage through a flame the individual particles of a dispersed powder will be heated and may partially evaporate. The heat transferred from the flame gases to the particles may not represent a significant thermal drain on the flame,

but the evaporated material may effect the combustion reactions. Two problems must be considered: the degree of heating of small particles by the flame, and the extent of evaporation resulting from this heating. The two problems are coupled and in their entirety are extremely difficult to solve. However, with some simplifying assumptions it is possible to obtain solutions which are adequate for our purposes.

The actual temperature profile through a premixed flame is replaced by the profile shown in Fig. 8, which has been divided into three zones: a preheat zone in which the temperature of the unburned gas rises exponentially with distance, a reaction zone in which the temperature rises linearly with distance, and a post-combustion zone of uniform temperature. The assumed temperature profile has been terminated at a definite position $x = \delta$, because where strong chemical inhibition occurs it must occur where the reaction rate is high, that is, in or near the visible flame. The reactions which take place in the post flame gases do so gradually over a distance large compared with the thickness of the visible flame. Particles in the region $x > \delta$ may affect these processes and will eventually reach thermodynamic equilibrium with the hot combustion gases. In this analysis, however, the region $x > \delta$ will not be considered. In addition, because the observed sensitivity of flame speed to the presence of some powders is far greater than can be accounted for by heat loss alone, the effect of the powder on T_a, the adiabatic flame temperature, has been neglected.

In the preheat zone the reaction rate is taken to be zero. Consequently, the temperature profile has the form (Ref. 6)

$$\frac{T_1 - T_i}{T_o - T_i} = \exp\left(\frac{c\rho_i\, Sx}{\lambda}\right) \tag{3}$$

where
ρ_i = the initial gas density

T_1 = the gas temperature at a point x

T_i = the initial gas temperature

T_o = an ignition temperature

c = the average heat capacity of the gas

λ = the average thermal conductivity of the gas

S = the flame speed

The preheat zone ends at the point $x = 0$, where $T_1 = T_o$. For mathematical convenience T_o is taken as the average of T_i and the adiabatic flame temperature T_a. The quantities c and λ should be values averaged over the temperature interval $T_o - T_i$. Because c and λ also appear in calculations for the reaction zone, it is more convenient to evaluate c and λ at T_o and use those values for both the preheat and the reaction zones.

The gas temperature in the reaction zone increases linearly from T_o to T_a and can be represented by the expression

$$\frac{T_1 - T_o}{T_o - T_i} = \frac{x}{\delta} \tag{4}$$

where $\delta = \dfrac{\lambda}{c\rho_i S}$. Equation 4 is the tangent to Eq. 3 at the point $x = 0$. As shown in Fig. 8, the parameter δ is the thickness of the reaction zone, about 0.2 mm for a stoichiometric CH_4-air flame.

In both the preheat and the reaction zones the time rate of temperature increase of nonevaporating spherical particle has been represented by Eq. 5.

$$\rho_s^{\cdot} c_s V_s \frac{dT}{dt} = 2\pi d\ \lambda(T_1 - T) \tag{5}$$

where
V_s = volume of the particle

d = diameter of the particle

T_1 = the gas temperature

T = the particle temperature

c_s = specific heat of the particle material

ρ_s = density of the particle

The most important assumptions implied by Eq. 5 are:

(1) The thermal conductivity of the particle material is very large, consequently the temperature within the particle is uniform and equal to the surface temperature

(2) The course of particle heating may be regarded as a succession of incremental steady states

(3) The Nusselt number for heat transfer equals 2.

These plausible assumptions simplify the mathematical problem but may introduce some error. The first of these assumptions is the least serious. A rigorous treatment of a related problem, the temperature history of a small particle of similar physical properties suddenly immersed in a large quantity of a hot gas, indicated that no significant error resulted from the assumption of uniform particle temperature.

A certain length of time is required to attain a steady state for either heat transfer or diffusion. For heat transfer, a measure of this time is the quantity $\ell^2/2\alpha$, where ℓ is some characteristic distance, and α is the thermal diffusivity of the gas. Similarly, for diffusion a measure of the time is the quantity $\ell^2/2D$ where D is the diffusion constant of the evaporating material through the surrounding medium. For this problem α and D are of comparable magnitude, a few cm²/sec. The characteristic distance ℓ may be taken as the radius of the particle. For particles with radii less than 5 microns the time required for attainment of a steady state (for either diffusion or heat transfer) is found to be less than 10^{-7} sec, compared to the transit time through the flame greater than 10^{-4} sec. It may be concluded that the steady state assumption involves little or no error.

The applicability of the steady state assumption for heat transfer is implied when using a value of two for the Nusselt number. In addition, only conductive heat transfer is taken into consideration. For the very small particles with which we are concerned this is probably the case.

The velocity of a particle being swept along by a moving gas will always differ from that of the gas itself. The importance of this lag can be estimated by comparing the relaxation time associated with velocity lag to the transit time of the particle through the flame. The relaxation time for velocity lag is given by the expression $\tau_v = \frac{2r^2\rho}{9\eta}$ where r = radius of the particle, ρ = density of the particle, η = viscosity of the surrounding gas. This time τ_v is the time required for a particle initially at rest in a quiescent gas to accelerate as a consequence of gravitational pull to $(1 - \frac{1}{e})$ of the terminal velocity. The lag time τ_v was evaluated for various values of r , with ρ = 2 gms/cc, and η = 490 μpoises (this value of η corresponds to air at about 1000°C). For

$r = 1\mu$, $\tau_v = 0.9 \times 10^{-5}$ sec, and for $r = 5\mu$, $\tau_v = 2.3 \times 10^{-4}$ sec. The transit times of interest are in the range 10^{-4} to 10^{-3} sec. It appears that velocity lag is not a serious perturbation for small particles ($r \sim 1$ or 2μ) but will occur to some extent for larger particles ($r \sim 5\mu$). The effect of velocity lag will be to lengthen the time of exposure of the particle to the flame. The rate of heat transfer will not be significantly affected because of the low Reynolds number associated with small particles and the relatively low gas velocities used. In these semi-quantitative calculations the effect of evaporation on drop and heat transfer is not taken into account.

Equation 5 may be converted to a form involving distance rather than time by means of the relation

$$\frac{dT}{dt} = \bar{v} \frac{dT}{dx} \tag{6}$$

where $\bar{v}$ is the average velocity of the gas-powder mixture. The use of a single average velocity for both gas and powder requires that the particles be small enough to follow the gas flow.

The integral of Eq. 6 for values of $x < 0$ is given by

$$\frac{T - T_i}{T_o - T_i} = \frac{\Phi\delta e^{x/\delta}}{1 + \Phi\delta} \tag{7}$$

where

$$\Phi = \frac{12 \lambda}{\bar{v} \, c_s \, \rho_s \, d^2} \tag{8}$$

Based on the conservation of mass equation the average flow velocity of the gas-powder mixture, $\bar{v}$, is approximately equal to $4S$ for near-stoichiometric CH_4-air flames. For values of $x > 0$, the integral of Eq. 6 is given by

$$T = T_o + (T_o - T_i) \left[\frac{e^{-\Phi\delta(\frac{x}{\delta})} + \Phi\delta(\frac{x}{\delta}) - 1}{\Phi\delta} - \frac{e^{-\Phi\delta(\frac{x}{\delta})}}{1 + \Phi\delta} \right] \tag{9}$$

and at $x = \delta$,

$$T_w = T_o + (T_o - T_i) \left[\frac{e^{-\Phi\delta} + \Phi\delta - 1}{\Phi\delta} - \frac{e^{-\Phi\delta}}{1 + \Phi\delta} \right] \tag{10}$$

The particle temperature within the reaction zone is seen to depend on the product parameter $\Phi\delta$ and on the dimensionless distance-ratio x/δ. The particle temperature at the end of the reaction zone is a function of $\Phi\delta$ alone.

The temperature T_w has been calculated as a function of particle size for these specific values: $c_s\rho_s = 2/3$ and 1, $\bar{v} = 4S$, $\lambda = 2 \times 10^{-4}$ cal cm^{-1} sec^{-1} deg^{-1}, $\rho_i = 1 \times 10^{-3}$ gms cm^{-3}, $c = 1/4$ cal gm^{-1} deg^{-1}, and $S = 40, 25, 15$, and 10 cm sec^{-1}. The cited values for $c_s\rho_s$ are applicable to NaCl and NaF, respectively. It is clear from the variation of T_w with particle size (Fig. 9) that the degree of particle heating can be great and that particle temperature can rise high enough to result in evaporation of materials not usually considered volatile.

In an isothermal system the steady state molar rate of flow, ψ_M, of material M diffusing away from a sphere of radius r may be represented by

$$\psi_M = -4\pi \, Drn\ell n \left(1 - \frac{n_1}{n}\right) \tag{11}$$

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where n = total molar concentration

          n_1 = molar concentration of "M" at the surface of the sphere

          D = diffusion constant of "M"

If the ratio $n_1/n \ll 1$, Eq. 11 may be approximated by

$$\psi_M = 4\pi \, Drn_1 \tag{12}$$

Relative to unevaporated material the enthalpy flow ψ_L associated with the molar flow, ψ_M, is given by

$$\psi_L = 4\pi \, Drn_1 L \tag{13}$$

where L is the molar heat of evaporation. In a nonisothermal system, such as a flame, the material diffusing away from a particle will be further heated as it diffuses. This enthalpy increase, however, is small compared with L which is about 40 to 50 kcal/mole for the materials we will consider and, therefore, it will be neglected. The diffusion and heat transfer processes are then coupled only at the surface of the particle. As in the case of heat transfer alone, it is assumed that steady state expressions can be used to describe the rate at which mass and heat are transferred.

    Evaporation (an endothermic process) is limited by, and can proceed only to, the extent that heat is provided to maintain the process. The rate of conductive heat transfer, q, from the flame gases to the particles is given by

$$q = 2\pi d\lambda \, (T_1 - T) \tag{14}$$

Initially, $q \gg \psi_L$, and both the particle temperature and n_1 increase. Eventually there may arrive a time when $q = \psi_L$ and evaporation may be regarded as having begun at that time. Further addition of heat to a particle will result primarily in evaporation and only secondarily in an increase in particle temperature. This temperature increase is not thermally significant but is important in that n_1 is a strongly varying function of particle temperature. The temperature at which evaporation may be considered to have begun can be obtained by equating Eqs. 13 and 14.

$$\lambda \, (T_1 - T) = n_1 \, L \, D \tag{15}$$

The quantity n_1 is related to particle temperature by

$$n_1 = A \, e^{-L/RT} \tag{16}$$

Equation 16 when substituted in Eq. 15 results in

$$T_1 - T = \frac{A \, e^{-L/RT} \, D \, L}{\lambda} \tag{17}$$

The initial evaporation temperature is that temperature T_e consistent with Eqs. 4, 9, and 17 (for $x > 0$).

    By graphical methods T_e was determined as a function of particle size for NaCl and NaF. The necessary thermodynamic data were obtained from Ref. 7 and used to derive expressions of the type Eq. 16 for n_1. For NaCl these data were used: B.P. = 1738°K, L at B.P. = 41 kcal/mole, D = 4 cm^2/sec. The quantity n_1 was represented by

$$n_1 = 0.924 \times 10^{-8900/T} \text{ moles/cc} \tag{18}$$

For NaF these data were used: B.P. = 1977°K, L = 48 kcal/mole, D = 4 cm^2/sec, and n_1 was represented by

$$n_1 = 1.12 \times 10^{-10,400/T} \text{ moles/cc} \tag{19}$$

In both cases the diffusion constant D is an estimated value.

The variation of T_e (initial) with particle size was determined graphically. Because S and r enter into the parameter Φ in the same way, once T_e is shown as a function of particle size for a given flame speed, T_e can readily be calculated as a function of size for other flame speeds. For either NaCl or NaF the initial evaporation temperature increases with increasing particle size up to a maximum value, $T_e(max)$. The temperature of an evaporating particle cannot exceed (although it will reach) $T_e(max)$ at $x = \delta$ unless the particle evaporates completely during passage through the flame. For NaCl, $T_e(max) = 1480°K$, and for NaF, $T_e(max) = 1650°K$.

Equation 12 implies that a particle evaporating under steady state conditions will decrease in size at a rate described by the expression

$$d^2 = d_0{}^2 - \frac{8\,M\,D\,n_1\,t}{\rho_s} \tag{20}$$

where $\quad\quad\quad\quad M = $ molecular wt of material.

A similar steady state expression can be derived for a particle evaporating in a flame

$$d^2 = d_0{}^2 - \frac{8\,M\,\lambda}{\rho_s\,L}\int_0^t (T_1 - T)\,dt \tag{21}$$

In Eq. 21, n_1 has been eliminated by means of Eq. 15. Time is measured from the onset of evaporation as previously defined. Let x_e be the point in the flame corresponding to this time. In the cases we will consider, $x_e > 0$. This distance will be traversed in a time $\tau = \delta - x_e)/\bar{v}$.

$$\frac{d_w{}^2}{d_0{}^2} = 1 - \frac{8\,M\,\lambda}{\rho_s\,L}\,(\overline{T_1 - T})\,\tau \tag{22}$$

where $\quad\quad\quad\quad d_w = $ diameter of the particle at $x = \delta$

$\quad\quad\quad(\overline{T_1 - T}) = $ the average temperature difference between the gas and the particle in the interval $\delta - x_e$.

Further, $\bar{v} = 4S$, and after substitution for τ and $\bar{v}$ and some manipulation, Eq. 22 can be transformed into Eq. 23, a form suitable for determining the degree of evaporation.

$$\frac{d_w{}^2}{d_0{}^2} = 1 - \frac{2\,M\,c_s\,(\Phi\delta)_0}{3'L}\left(1 - \frac{x_e}{\delta}\right)(\overline{T_1 - T}) \tag{23}$$

The parameter $(\Phi\delta)_0$ is the value of $\Phi\delta$ appropriate to d_0 and to an assumed value of the flame speed. The quantity $1 - \frac{x_e}{\delta}$ can be obtained from a graph of $(T_1 - T_e)_i$ as a function of $(\Phi\delta)_0$, the value of $(\Phi\delta)_0$, and Eq. 4. The quantity $(\overline{T_1 - T})$ may be taken without significant error as the average of $(T_1 - T_e)_i$ at $x = x_e$ and $(T_1 - T_e)_f$ at $x = \delta$. For NaCl, $(T_1 - T_e)_f = 720°K$ and for NaF, $(T_1 - T_e)_f = 550°K$.

Proceeding as indicated, we calculated the fractional degree of evaporation, $f = 1 - \frac{d_w{}^3}{d_0{}^3}$, for NaCl and NaF. The results are shown in Fig. 10. The product Sd_0 is constant for a given degree of evaporation. Consequently, the variation of f with particle size for any flame speed can be easily obtained once the variation is known for a single flame speed.

The calculation of degree of evaporation carried out for $x = \delta$ can be done for other selected values of x. For the purpose of demonstrating that small

particles of materials such as NaCl and NaF will partially evaporate during passage through a flame, the results shown in Fig. 10 for $x = \delta$ are sufficient.

The mathematical analysis just described can only be successfully applied to materials for which there is available a relation between the vapor pressure and the temperature of the material. Substances such as Na_2CO_3 which decompose during evaporation cannot be treated. Therefore, the relative volatility of several such materials was determined in the following way. A small quantity of material was fused by flame onto the end of a platinum wire until a small bead about 1 mm in diameter had been formed. The bead and wire were suspended in a Meker burner flame about 1 cm above the primary cones. By stopwatch, the time was measured from the appearance of color in the flame gases to the disappearance of that color. The results of such measurements are shown in Table II.

Consideration of the data in Table II reveals a number of interesting facts. NaF and Na_2CO_3 have roughly the same volatility. Consequently, the degree of evaporation derived for NaF can be expected to apply roughly to Na_2CO_3 as well. Next, K_2CO_3 is seen to be about twice as volatile as Na_2CO_3. This is also about the same as the ratio of inhibition effectiveness for these two materials. Lastly, all the test substances except Na_2CO_3 are more volatile than NaF and small particles of these substances would be expected to evaporate during passage through a flame to an even greater extent than NaF particles of the same size. Powders of all but two of the materials listed in Table II were tested experimentally and found to be effective inhibitors of CH_4-air combustion. Materials which were not effective inhibitors, talc, $CaCO_3$, $Ca(OH)_2$, and CaF_2 are not volatile at the flame temperatures encountered in our system and would not be expected to evaporate to a significant extent during passage through a CH_4-air flame although $CaCO_3$ and $Ca(OH)_2$ might decompose to CaO. It appears that evaporation and inhibition effectiveness are companions and that the observed inhibition is due to evaporated materials. With increasing flame temperature some of these less volatile materials may exhibit a higher degree of effectiveness.

IV. Discussion

The theoretical analysis presented in Section III revealed that a significant amount of evaporation will occur for those powders which were found to be effective inhibitors. The extent of evaporation will depend on the temperature history of the powder particles and on the volatility of the material. The calculated results for NaCl and NaF shown in Fig. 10 indicate a high degree of evaporation by the end of the reaction zone. The average extent of evaporation in the reaction zone will be lower. For all but the very finest powders the degree of evaporation for the spectrum of particle sizes present in the powder is probably much less than one. Under such conditions one would expect a proportionality between powder effectiveness and specific surface area. An increase in specific surface area will result in greater fractional evaporation. Evaporation can, of course, be completed in the post flame gases, but we are not concerned with that region -- only with the reaction zone itself.

Two essential tasks remain: to identify the species responsible for inhibition and the reactions involved. To that end, consider first the relatively simple case of NaCl. The condensed material will evaporate at high temperatures primarily as NaCl molecules. The NaCl in diffusing through the hot reaction gases may be converted to Na by reactions such as
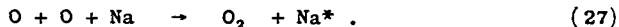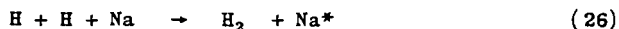
$$H + NaCl \rightarrow Na = HCl \qquad (24)$$

Experimental observation of flames in which Na and Cl were both present indicates that the conversion will not be complete (Ref. 8). Consequently, both Na

and NaCl must be accepted as major species involving Na . Traces of NaOH can also be present, as well as minute concentrations of sodium hydride or sodium oxides. However, the oxides have never been observed spectroscopically in flames which also contained sodium (Ref. 9). Inasmuch as only minute concentrations are required to give observeable emission spectra, the presence of significant quantities of these compounds is unlikely. As far as NaCl is concerned, the major species to consider are Na and NaCl.

Consider next the more complicated case of Na_2CO_3 which evaporates with decomposition. Depending on the circumstances one may initially have Na, Na_2O, Na_2O_2, etc. The initial spectrum of products in the course of diffusing away from the particle will be altered. The major species to be expected at some distance from the particle is the Na atom. The presence of chlorine species in the gas will convert a portion of that sodium into NaCl . The observed decrease in powder effectiveness as observed in the presence of Na_2CO_3 powder and CH_3Cl (see Fig. 7) indicates that NaCl is relatively inactive and that inhibition is associated with the sodium atom. By implication the overall effectiveness of a sodium compound depends not only on volatility but also on the availability of the atom after evaporation. By analogy other alkali metal compounds would behave similarly. The ability to inhibit combustion is probably not limited to the alkali metal atoms in view of the similar results obtained with NaCl and CuCl: The two are of comparable volatility and both would yield some metal atoms, Na in the one case and Cu in the other. Further, both $Pb(C_2H_5)_4$ and $Fe(CO)_5$ strongly inhibit hexane-air flames (Ref. 10). A metal atom mechanism may be operative in those cases too, although both Fe and Pb may be partially converted to oxides or hydroxides.

The second task is to identify a mechanism of inhibition which depends on the presence of metal atoms. A number of possible mechanisms were considered. Of these, three were found to be consistent with the obtained results.

It is possible that metal atoms increase the rate of recombination of the radicals directly associated with flame propagation -- H, O , and OH. Recombination reactions limit the concentration of radicals in the flame and insure their removal in the post flame gases. Consequently, an increase in recombination rate can be expected to reduce flame speed. A metal such as Na , which we will use as an example, can affect recombination rate by acting as a third body which is efficient in absorbing a portion of the energy of recombination.

$$H + OH + Na \rightarrow H_2O + Na* \qquad (25)$$

$$H + H + Na \rightarrow H_2 + Na* \qquad (26)$$

$$O + O + Na \rightarrow O_2 + Na* . \qquad (27)$$

The efficiency of Na as a third body in reactions 25 and 26 has been measured in flame gases (Ref. 11) but is not greater than that of other flame components present in far larger concentrations. Therefore, little direct effect can be expected. However, Na does remove at least 50 kcal of energy, the excitation energy for the transition $Na(^2S) \rightarrow Na*(^2P)$. This excitation energy may then be radiated as light or degraded into heat by collision with other molecules. On the other hand, such third bodies as the product molecules H_2O, H_2, or O_2 may absorb all or a portion of the energy released in recombination reactions of the type shown in Eqs. 25, 26, and 27. Such molecules with excess energy may be of unusual chemical reactivity. However, in the case of vibrationally excited product molecules collisions with other molecules will lead to rapid loss of this energy. The mechanism cited cannot be definitely ruled out on the basis of our present knowledge about the state of excitation of the products resulting from recombination reactions.

A metal such as Na can also alter a rate of recombination by a two-step process like that shown formally in Eqs. 28 and 29.

$$A + Na + M \rightarrow A - Na + M \qquad (28)$$
$$B + A - Na \rightarrow A - B + Na \qquad (29)$$
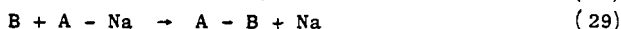
in which A and B are H, O, and OH, and M is a third body. The collision-stabilized complex Na-A need not be a major species but it must have a sufficient lifetime to react with B. Such a mechanism has recently been advanced as an explanation of third-body efficiencies and negative temperature coefficients (Refs. 12 and 13). If the product molecule Na-A does survive this length of time and if reaction 29 is exothermic, the rate of reactions 28-29 relative to the direct recombination

$$A + B + M \rightarrow A - B + M \qquad (30)$$

will be about equal to the ratio Na/B. In order to evaluate the feasibility of this mechanism the cited ratio must accordingly be known.

The equilibrium mole fractions of H, OH, O in the post flame gases of a one-atmosphere stoichiometric CH_4-air flame are known (Ref. 14).

$$T_a = 2214^{\circ}K$$

Equilibrium Mole Fraction $\begin{cases} H &= 3.57 \times 10^{-4} \\ OH &= 27.8 \times 10^{-4} \\ O &= 2.11 \times 10^{-4} \end{cases}$

In the flame zone itself the mole fractions of these three species are undoubtedly much higher, consequently the cited values represent lower limits. The concentration of Na in an inhibited flame can be estimated from the data shown in Fig. 2 for fine Na_2CO_3. About 0.003 mg/cc reduces propagation velocity by about half of the original value. The mole fraction of Na corresponding to that concentration is about 1.5×10^{-3}. If the average degree of evaporation in the flame is about 10%, the mole fraction of Na in the gas will be 1.5×10^{-4}. A higher degree of evaporation is unlikely in view of the proportionality between specific surface area and powder effectiveness. Comparison of the mole fraction of Na in the flame with the lower limit values for H, OH, and O indicates that the ratio Na/B in the flame is probably much less than one. In the post flame gases, the degree of evaporation is much higher and the concentration of radicals lower. In that region the mechanism is a feasible one, although it is apparently not feasible in the reaction zone unless the estimates of concentration are badly in error.

Finally, Na may deactivate energetically excited species such as O_2^*, CO_2^*, C_2^*, CH^*, OH^*. The concentration in the flame of each of the cited species is not known but is probably low. These species may in addition be sideshow performers not directly involved in flame propagation. Consider for instance C_2^* and CH^*. Emission intensities from C_2^* and CH^* increases with the addition of bromine inhibitors (Ref. 15), although flame speed decreases. Both C_2^* and CH^* are apparently unrelated to flame speed. On the other hand, emission intensity of OH^* decreases with increasing concentration of bromine inhibitor (Ref. 15). However, OH^* is deexcited on virtually every collision with flame gases (Ref. 16). Consequently, a minor constituent can have little further influence on the deactivation of OH^*. The decrease in emission intensity is probably associated with a diminution in the rate of production of OH^* upon the addition of an inhibitor rather than its removal by reaction with HBr (Ref. 15).
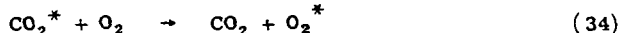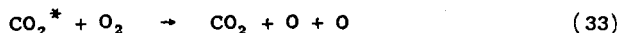
Inhibition can result from the deactivation of CO_2^*. The reactants necessary to form CO_2^* are present in the flame, such as

$$O + CO \xrightarrow{M} CO_2^* \tag{31}$$

Moreover, CO_2^* is metastable with respect to radiation because of the multiplicity change associated with the radiative transition (Ref. 17),
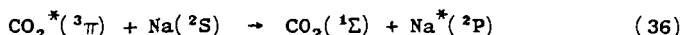
$$CO_2^*(^3\pi) \rightarrow CO_2(^1\Sigma) + h\nu . \tag{32}$$
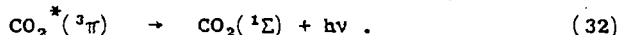
Excited CO_2^* can therefore exist for a time and be available for reactions such as those shown (Ref. 17)

$$CO_2^* + O_2 \rightarrow CO_2 + O + O \tag{33}$$

$$CO_2^* + O_2 \rightarrow CO_2 + O_2^* \tag{34}$$

$$O_2^* + CO \rightarrow CO_2 + O \tag{35}$$

Oxygen atoms produced by reactions 33 and 35 may by further reaction produce H and OH.

If Na (or other metal atom) is present in the flame the deexcitation reaction

$$CO_2^*(^3\pi) + Na(^2S) \rightarrow CO_2(^1\Sigma) + Na^*(^2P) \tag{36}$$

could remove the energy required for reaction 33. The excitation energy of $Na^*(^2P)$ may be radiated or eventually degraded into thermal energy by collision. The excited O_2^* formed in reaction 34 can also lose its energy of excitation by colli-with Na, expecially if the O_2 is only vibrationally excited (Ref. 18). This mechanism of inhibition, the removal of excitation energy by metal atoms, provides a qualitative explanation for metal inhibition. So far as know, it is consistent with fact. The mechanism does require that CO_2^* be an important intermediate in the combustion of hydrocarbons.

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Table I

SPECIFIC AREA OF POWDERS USED

Powder	$A^*(cm^2/gm)$	$\bar{d}(\mu)$
talc	12,600	2.4
$Ca(OH)_2$	9,000	2.9
$CaCO_3$	2,000	11
NaBr	2,000	9
CaF_2	3,500	5.4
NaF	3,300	6.5
CuCl	3,000	5.7
NaCl	4,500	6.0
K_2SO_4	5,200	4.3
$NaHCO_3$	7,760	3.5
$NaHCO_3$	11,900	2.3
$KHCO_3$	12,400	2.2
Na_2CO_3	4,940	4.9
Na_2CO_3	10,800	2.2

$$\bar{d} = \frac{6}{\rho A^*}$$

$\bar{d}$ = average particle diameter

ρ = density of material

A^* = specific surface area

Table II

RELATIVE VOLATILITY OF VARIOUS SOLIDS

Substance	τ (sec)	B.P. (^oK)
NaI	~ 1	1577
KCl	~ 2	1680
CuCl	~ 2	1639
NaBr	~ 2	1666
NaCl	3	1738
K_2CO_3	7	....
K_2SO_4	10	....
Li_2CO_3	11	....
NaF	13	1977
Na_2CO_3	16	....

τ = lifetime of 1 mm bead of material when exposed to a Meker flame
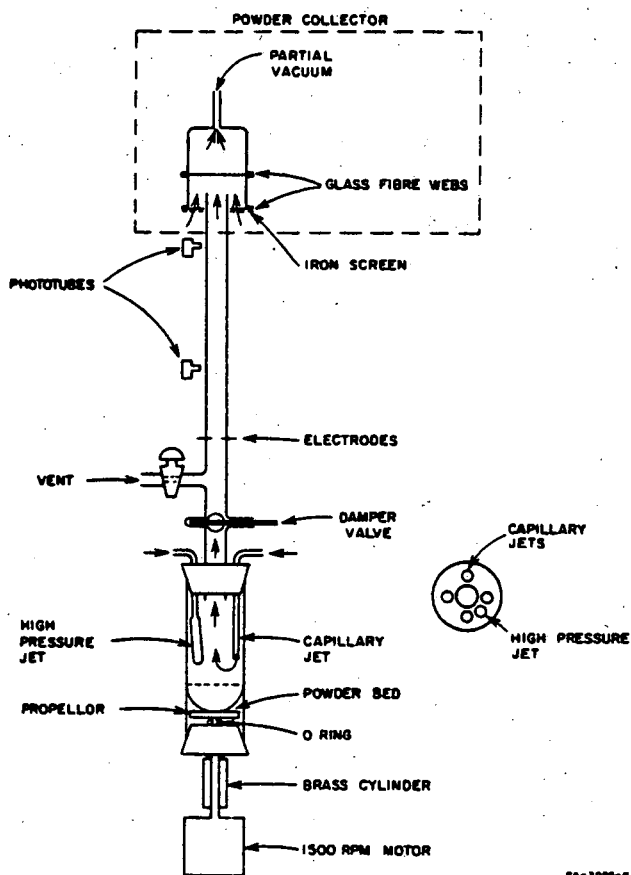
FIG. 1

POWDER GENERATOR AND FLAME TUBE
SCHEMATIC DIAGRAM
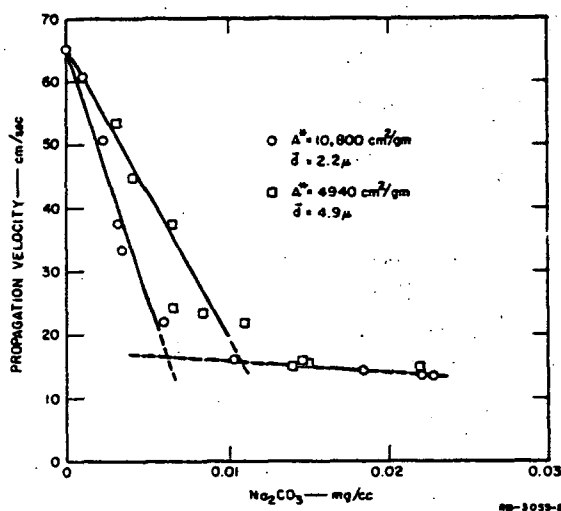
FIG. 2

STOICHIOMETRIC CH_4-AIR: THE EFFECT OF Na_2CO_3
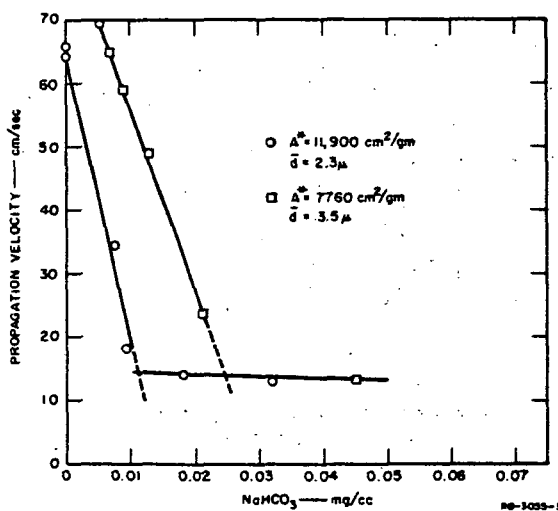ON THE PROPAGATION VELOCITY

FIG. 3

STOICHIOMETRIC CH_4-AIR — EFFECT OF $NaHCO_3$
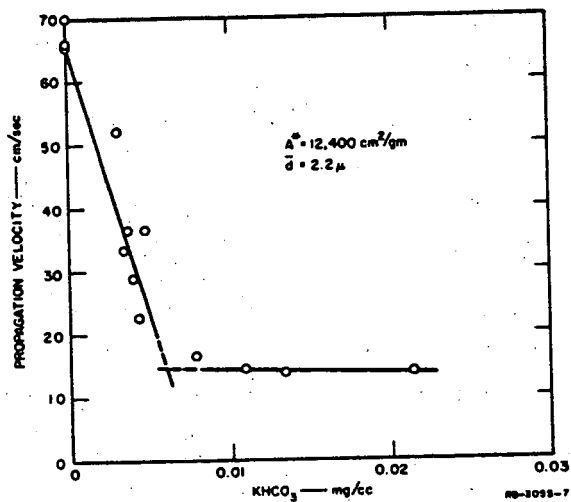ON PROPAGATION VELOCITY

FIG. 4

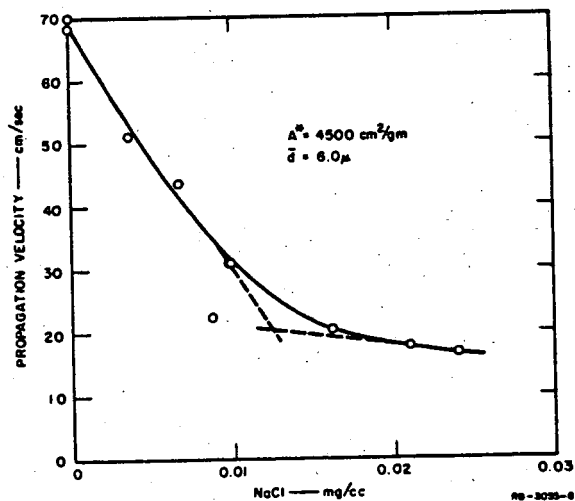STOICHIOMETRIC CH$_4$-AIR — EFFECT OF KHCO$_3$
ON PROPAGATION VELOCITY

FIG. 5

STOICHIOMETRIC CH$_4$-AIR — EFFECT OF NaCl
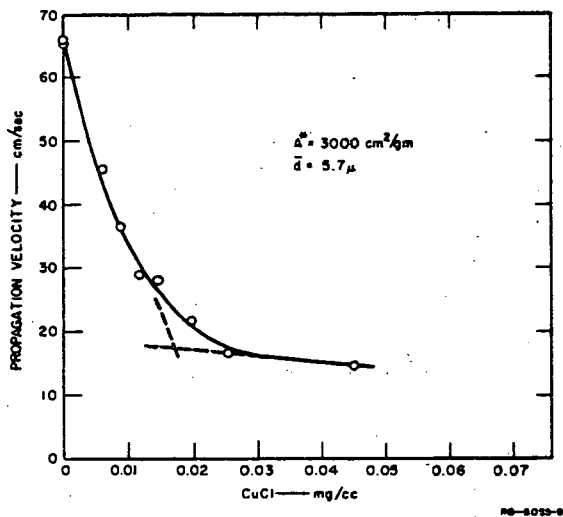ON PROPAGATION VELOCITY

FIG. 6

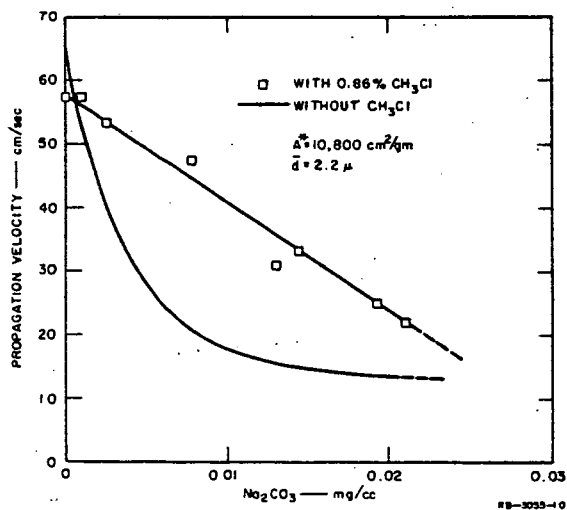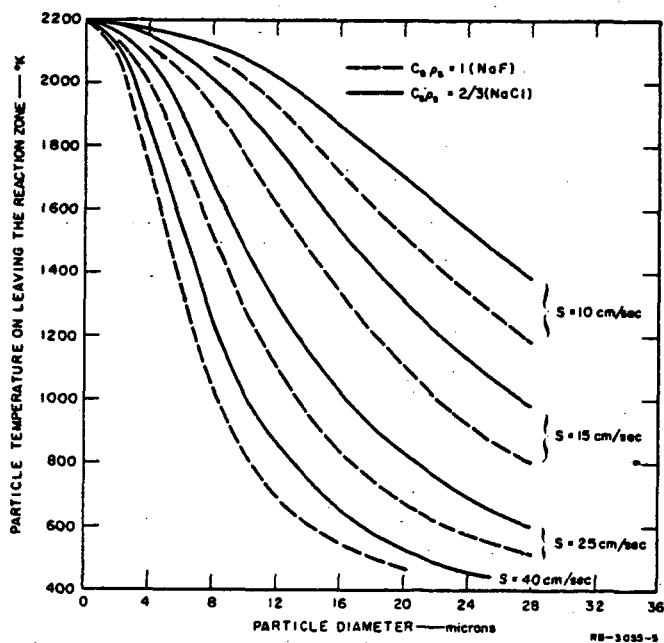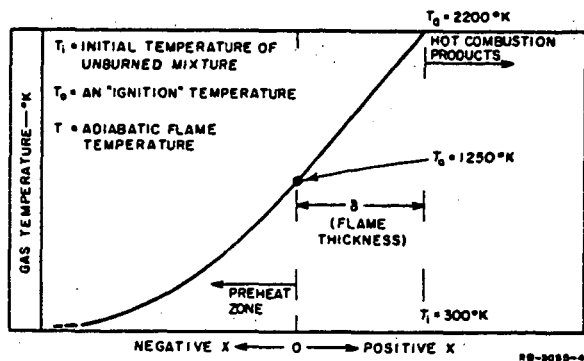STOICHIOMETRIC CH$_4$-AIR — EFFECT OF CuCl
ON PROPAGATION VELOCITY

FIG. 7

STOICHIOMETRIC CH$_4$-AIR — THE EFFECT OF CH$_3$Cl
ON THE EFFECTIVENESS OF Na$_2$CO$_3$

FIG. 8

ASSUMED TEMPERATURE PROFILE FOR A STOICHIOMETRIC
CH₄-AIR FLAME

FIG. 9

THE TEMPERATURE REACHED BY SMALL NONEVAPORATING PARTICLES
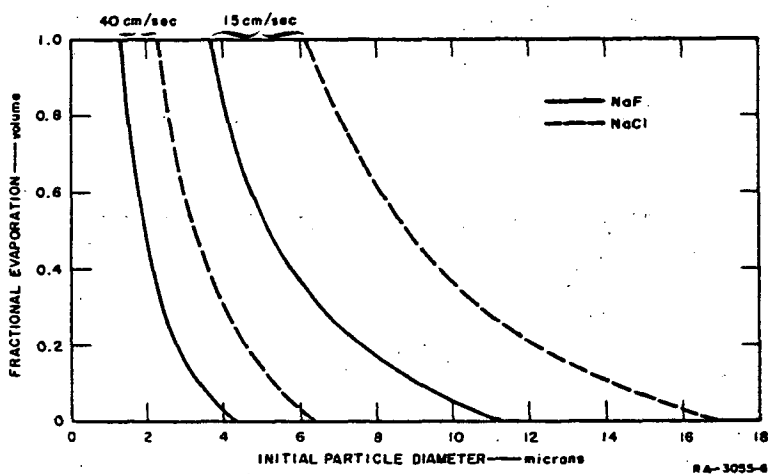DURING PASSAGE THROUGH A STOICHIOMETRIC CH₄-AIR FLAME

FIG. 10

FRACTIONAL EVAPORATION OF NaCl AND OF NaF
ON LEAVING THE REACTION ZONE